

Redistribution/Dehydrocoupling of Tertiary Alkylstannane $n\text{-Bu}_3\text{SnH}$ Catalyzed by Group 4 and 6 Transition Metal Complexes

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The catalytic transformation of sterically bulky tertiary stannane $n\text{-Bu}_3\text{SnH}$ by the $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M}=\text{Ti, Zr, Hf}$) and $\text{M}(\text{CO})_6$ ($\text{M}=\text{Cr, Mo, W}$) catalysts yielded two kinds of catenated products: one is a cross-linked polystannane as minor product, and the other is hexabutyldistannane ($n\text{-Bu}_3\text{Sn}$)₂ as major product. The distannane was produced by simple dehydrocoupling of $n\text{-Bu}_3\text{SnH}$, whereas the cross-linked polystannane could be obtained *via* redistribution/dehydrocoupling combination process of $n\text{-Bu}_3\text{SnH}$. The redistribution/dehydrocoupling combination process may initially produce a low-molecular-weight oligostannane with partial backbone Sn-H bonds which could then undergo an extensive cross-linking reaction of backbone Sn-H bonds, resulting in the formation of an insoluble polystannane.

Introduction

Among inorganic polymers possessing various superior properties over organic polymers,¹ polysilanes with unique optoelectronic and chemical properties attributed to σ electron-conjugation along the one-dimensional silicon polymer backbone have received a great deal of attention.² The conventional Wurtz coupling reaction of organodichlorosilanes using an alkali metal dispersion in toluene-refluxing temperature for synthesizing polysilanes has several disadvantages.³ Synthetic alternative methods for synthesizing polysilanes without resort to a transition metal catalyst have been reported.⁴ *Inter alia*, Harrod's recent discovery of a group 4 metallocene-catalyzed dehydropolymerization of hydrosilanes, paved the revolutionary way to synthesize polysilanes.⁵ Worldwide efforts have been intensively made to refine the dehydropolymerization method.⁶⁻¹¹

Compared to polysilane, polystannane, a tin analogue of polysilane, has not been studied until quite recently because of its synthetic difficulties. The synthesis of poly(*n*-butylstannane)s by Wurtz-type coupling of $n\text{-Bu}_2\text{SnCl}_2$ using molten Na metal¹² and by hydrostannolysis of $n\text{-Bu}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{OEt})\text{NMe}_2$ in the presence of DIBAL-H¹³ have been reported. Recently, Tilley *et al.* described the catalytic dehydropolymerization of secondary stannanes by the group 4 zirconocene complexes, producing soluble (uncross-linked) mixtures of cyclic oligostannanes (up to 50%) and linear polystannanes (M_w up to 70000).^{14a,b} Subsequently, Corey and coworker reported the similar dehydropolymerization of $n\text{-Bu}_2\text{SnH}_2$ catalyzed by the $\text{Cp}_2\text{MCl}_2/n\text{-BuLi}$ ($\text{M}=\text{Zr, Hf}$) combination.^{14c} The group 4 $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M}=\text{Ti, Zr, Hf}$) combination catalyst and the group 6 $\text{M}(\text{CO})_6$ ($\text{M}=\text{Cr, Mo, W}$) catalyst have been developed in our laboratory for dehydropolymerization of hydrosilanes to polysilanes.^{11,15} We very recently reported the redistribution/dehydropolymerization of secondary alkylstannane $n\text{-Bu}_2\text{SnH}_2$ catalyzed by the $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M}=\text{Zr, Hf}$) and $\text{M}(\text{CO})_6/\text{Red-Al}$ ($\text{M}=\text{Cr, Mo, W}$) combinations, producing cross-linked insoluble polystannanes and non-cross-linked soluble oligostannanes.¹⁶ Here we wish to report our study on the redistribution/dehydrocoupling of tertiary alkylstannane $n\text{-Bu}_3\text{SnH}$ cata-

lyzed by the group 4 $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M}=\text{Ti, Zr, Hf}$) combination and by the group 6 $\text{M}(\text{CO})_6$ ($\text{M}=\text{Cr, Mo, W}$) to compare their catalytic effects.

Experimental Section

All reactions and manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Infrared spectra were obtained using a Perkin-Elmer 1600 Series FT-IR or a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recorded on a Varian Gemini 300 spectrometer using $\text{CDCl}_3/\text{CHCl}_3$ as a reference at 7.24 ppm downfield from TMS. GC/MS data were obtained using a Hewlett Packard 5890II chromatograph (HP-5, 5% phenylmethylsiloxane, 0.25 mm id \times 30.0 m, film thickness 0.25 μm) connected to a Hewlett Packard 5972A mass selective detector. Thermogravimetric analysis (TGA) of the polymer sample was performed on a Perkin-Elmer 7 Series thermal analysis system under an argon flow. The polymer sample was heated from 25 to 900 $^\circ\text{C}$ at a rate of 20 $^\circ\text{C}/\text{min}$. Ceramic residue yield is reported as the percentage of the sample remaining after completion of the heating cycle. Cp_2MCl_2 ($\text{M}=\text{Ti, Zr, Hf}$), $\text{M}(\text{CO})_6$ ($\text{M}=\text{Cr, Mo, W}$), $n\text{-Bu}_3\text{SnCl}$, and Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride; 3.4 M in toluene) were purchased from Aldrich Chemical Co. and were used without further purification. $n\text{-Bu}_3\text{SnH}$ [IR (neat, KBr, cm^{-1}): 1808 s ($\nu_{\text{Sn-H}}$); ^1H NMR (δ , CDCl_3 , 300 MHz): 0.88 (t, $J=7.3$ Hz, 9H, $\text{Sn-CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.25 (m, 12H, $\text{Sn-CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.59 (m, 6H, $\text{Sn-CH}_2(\text{CH}_2)_2\text{CH}_3$), 5.22 (m, 1H, Sn-H)] was prepared before use by reduction of $n\text{-Bu}_3\text{SnCl}$ with LiAlH_4 in diethyl ether.¹⁷

Redistribution/Dehydrocoupling of $n\text{-Bu}_3\text{SnH}$ Catalyzed by $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M}=\text{Ti, Zr, Hf}$). The following procedure is the representative of redistribution/dehydrocoupling of $n\text{-Bu}_3\text{SnH}$ with the group 4 metallocene $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M}=\text{Ti, Zr, Hf}$) combination catalysts. $n\text{-Bu}_3\text{SnH}$ (0.50 g, 0.86 mmol) was added to a Schlenk flask containing *in situ*-generated dark purple catalytic mixture of Cp_2TiCl_2 (6.5 mg, 0.026 mmol) and Red-Al (6.7 μL , 0.026

mmol) which was protected from fluorescent room light because the products might be photochemically sensitive. The violet reaction mixture was heated at 70 °C to turn green instantly, and the reaction medium became slowly viscous. The catalyst was inactivated 72 h later by exposure to the air for a few minutes. The translucent viscous material with yellow-orange hue was washed well with dry THF and dried at reduced pressure to give 0.085 g (17% yield) of a pale yellow solid which was insoluble in most organic solvents. The combined washing solutions were pumped to dryness and the resulting oil was passed rapidly through a reverse phase silica gel column (70-230 mesh, 20 cm × 2 cm) with 100 mL of hexane used as the eluent. The effluent was evaporated *in vacuo* to yield 0.384 g (77% yield) of a clear pale yellow oil. For the solid: IR (KBr pellet, cm⁻¹): 1808 w (ν_{Sn-H}); TGA ceramic residue yield: 38% at 400 °C and 33% at 900 °C (grey solid), onset temperature for decomposition=300 °C. For the oil: IR (neat, KBr, cm⁻¹): ν_{Sn-H}-absent; ¹H NMR (δ, CDCl₃, 300 MHz): 0.85 (t, *J*=7.3 Hz, 18H, Sn-CH₂(CH₂)₂CH₃), 1.26 (m, 24H, Sn-CH₂(CH₂)₂-CH₃), 1.50 (m, 12H, Sn-CH₂(CH₂)₂CH₃); GC/MS, *m/e* (relative intensity): 581 (0.5, M⁺), 425 (8, Bu₃SnOSnBu⁺), 289 (30, Bu₃Sn⁺), 233 (42, Bu₂Sn⁺), 177 (100, BuSnH⁺), 133 (95, CH₂Sn⁺).

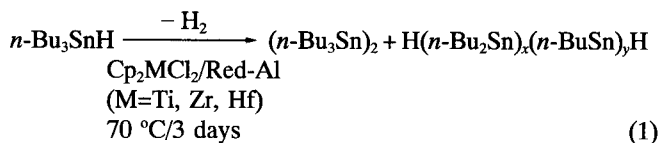
Redistribution/Dehydrocoupling of *n*-Bu₃SnH Catalyzed by M(CO)₆ (M=Cr, Mo, W). As a typical redistribution/dehydrocoupling of *n*-Bu₃SnH with the group 6 metal carbonyl M(CO)₆ (M=Cr, Mo, W) catalysts, a Schlenk flask was charged with *n*-Bu₃SnH (0.50 g, 0.86 mmol), Cr(CO)₆ (5.7 mg, 0.026 mmol), and dioxane (0.5 mL), keeping fluorescent room light avoided because the products and catalyst might be photochemically sensitive. The reaction mixture was slowly heated up to 90 °C in order to minimize the sublimation of Cr(CO)₆, and turned green. The catalyst was destroyed 72 h later by exposure to the air for a few minutes. The translucent viscous material with green color was washed well with dry THF and dried at reduced pressure to give 0.115 g (23% yield) of a pale green solid which was insoluble in most organic solvents. The combined washing solutions were pumped out and the resulting oil was passed rapidly through a reverse phase silica gel column (70-230 mesh, 20 cm × 2 cm) with 100 mL of hexane. The effluent was removed under vacuum to give 0.343 g (69% yield) of a clear pale yellow oil. For the solid: IR (KBr pellet, cm⁻¹): 1808 w (ν_{Sn-H}); TGA ceramic residue yield: 38% at 400 °C and 33% at 900 °C (grey solid), onset temperature for decomposition=300 °C. For the oil: IR (neat, KBr, cm⁻¹): ν_{Sn-H}-absent; ¹H NMR (δ, CDCl₃, 300 MHz): 0.85 (t, *J*=7.3 Hz, 18H, Sn-CH₂(CH₂)₂CH₃), 1.26 (m, 24H, Sn-CH₂(CH₂)₂CH₃), 1.50 (m, 12H, Sn-CH₂(CH₂)₂CH₃); GC/MS, *m/e* (relative intensity): 581 (0.5, M⁺), 425 (8, Bu₃SnOSnBu⁺), 289 (30, Bu₃Sn⁺), 233 (42, Bu₂Sn⁺), 177 (100, BuSnH⁺), 133 (95, CH₂Sn⁺).

Results and Discussion

Among group 4 metallocenes^{5,6,18} previously examined, CpCp*Zr[Si(SiMe₃)₃]Me and (CpCp*ZrH₂)₂ are the most active catalyst for the dehydropolymerization of primary silanes. However, the shelf life of the zirconocenes is short because the zirconocenes are thermally and photochemically

unstable even at -10 °C. Therefore, we used the *in situ*-generated combination catalysts, Cp₂MCl₂/Red-Al (M=Ti, Zr, Hf) which were recently found to give predominantly linear, higher molecular weight of polysilanes than for any other catalyst system.¹⁹ There is no single report up to date of dehydrocoupling of tertiary silanes catalyzed by early transition metal complexes. The dehydrocoupling reactivity of hydrosilanes is well known to decrease drastically in the order of primary > secondary >>> tertiary.¹⁰ A hydrostannane is more reactive toward various reactants than a hydrosilane²⁰ because the bond energy of Sn-H bond (74 kcal/mol) is smaller than that of Si-H bond (90 kcal/mol).²¹ In fact, Tilley *et al.* reported the dehydropolymerization of sterically hindered secondary stannanes catalyzed by the group 4 zirconocene complexes, producing a THF-soluble mixture of cyclic oligostannanes (up to 50%) and linear polystannanes (M_w up to 70000).¹⁴ We also decided to use another catalyst, M(CO)₆ (M=Cr, Mo, W) for the dehydrocoupling of *n*-Bu₃SnH in view of the fact that the group 6 transition metal carbonyl catalysts produce higher-molecular-weight polysilanes in the dehydrocoupling of alkylsilanes than the group 4 metallocene catalysts do.^{15c}

Dehydrocoupling of *n*-Bu₃SnH with 3 mol% of the Cp₂MCl₂/Red-Al (M=Ti, Zr, Hf) combination catalysts took place very slowly at ambient temperature, and upon heating at 70 °C the reaction medium became slowly viscous over 3 days (eq 1).



The products were isolated in high yield as two phases after workup including washing and flash chromatography. Hexabutylstannane, (n-Bu₃Sn)₂, was obtained in 77-82% yield as a clear pale yellow oil. Polystannane was acquired in 13-17% yield as a pale yellow solid which was insoluble in most organic solvents. The TGA ceramic residue yields at 900 °C of the insoluble solids were *ca.* 33%. The catalytic redistribution/dehydrocoupling reactions of *n*-Bu₃SnH with the group 4 metallocene combinations are summarized in Table 1.

The IR spectra of the polymeric solids exhibit a very weak ν_{Sn-H} band at 1808 cm⁻¹. The ¹H NMR spectra of (n-Bu₃Sn)₂ show resonances centered at 0.85, 1.26, 1.50 ppm assigned to CH₃, CH₂CH₂, and Sn-CH₂, respectively. The IR spectra of the hexabutylstannane do not exhibit a ν_{Sn-H} band at 1808 cm⁻¹. The mass spectra of the hexabutyl-

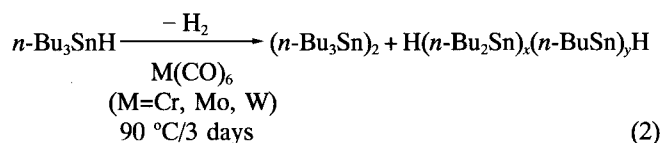
Table 1. Characterization of Catalytic Redistribution/Dehydrocoupling of *n*-Bu₃SnH with Group 4 Transition Metal Complex^a

Catalyst	% yield	
	Sn ₂ ^b	Sn _x ^c
Cp ₂ TiCl ₂ /Red-Al	77	17
Cp ₂ ZrCl ₂ /Red-Al	81	14
Cp ₂ HfCl ₂ /Red-Al	82	13

^a [M]/[Sn]=0.03; heating at 70 °C for 3 days. ^b Yield of THF-soluble product. ^c Yield of THF-insoluble product.

distannane show fragmentations of 581 (0.5, M⁺), 425 (8, Bu₃SnOSnBu⁺), 289 (30, Bu₃Sn⁺), 233 (42, Bu₂Sn⁺), 177 (100, BuSnH⁺), and 133 (95, CH₂Sn⁺). The clear pale yellow oily products were clearly identified as hexabutyldistannane by comparing with the ¹H NMR, IR, MS spectral data of authentic sample independently prepared according the literature procedure.²² However, as seen in the MS fragmentation pattern, the hexabutyldistannane was contaminated with small amount of (*n*-Bu₃Sn)₂O. (*n*-Bu₃Sn)₂ can be easily oxidized to (*n*-Bu₃Sn)₂O in the presence of moisture.²²

Similarly, redistribution/dehydrocoupling of *n*-Bu₃SnH with 3 mol% of the M(CO)₆ (M=Cr, Mo, W) catalyst commenced very slowly, and the reaction medium became slowly viscous upon heating at 90 °C over 3 days (eq 2).



The products were isolated in high yield as two phases after workup including washing and flash chromatography. Hexabutyldistannane was obtained in 69-90% yield as a clear pale yellow oil. Polystannane was acquired in 7-23% yield as a pale green solid which was insoluble in most organic solvents. The catalytic redistribution/dehydrocoupling reactions of *n*-Bu₃SnH with the group 6 metal carbonyls are given in Table 2.

The spectral data of the polymeric solids and oily products obtained with the group 6 metal carbonyl catalysts were same as those of the polymeric solids and oily products prepared with the group 4 metallocene combination catalysts.

We first expected that the catalytic dehydrocoupling of the sterically bulky *n*-Bu₃SnH by the group 4 and 6 transition metal complex could occur hardly to produce single product, (*n*-Bu₃Sn)₂ because the dehydrocoupling reactivity of hydrosilanes is well known to decrease drastically in the order of primary > secondary >>> tertiary.¹⁰ As shown in Table 1 and Table 2, the group 4 metallocene combination catalysts and the group 6 metal carbonyl catalysts in the dehydrocoupling of *n*-Bu₃SnH produce the expected dehydrocoupling product, (*n*-Bu₃Sn)₂, as a major product along with the unexpected redistribution/dehydrocoupling product, cross-linked insoluble polystannane, as a minor product. Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride) is known to catalyze the exchange reactions of di- and trihydrosilanes^{23a} and the oligomerization of disilanes,^{23b} catalyzed by inorganic hydrides (e.g., NaH, KH, etc.). Corriu *et al.* suggested a

Table 2. Characterization of Catalytic Redistribution/Dehydrocoupling of *n*-Bu₃SnH with Group 6 Transition Metal Complex^a

Catalyst	% yield	
	Sn ₂ ^b	Sn _x ^c
Cr(CO) ₆	69	23
Mo(CO) ₆	69	23
W(CO) ₆	90	7

^a [M]/[Sn]=0.03; heating at 90 °C for 3 days. ^b Yield of THF-soluble product. ^c Yield of THF-insoluble product.

mechanism *via* the intermediacy of a pentacoordinated hydrosilyl anion,^{23c} which is formed by addition of hydride (H⁻) on the silanes. We recently found an intriguing redistribution of bis- and tris(silyl)methanes with Si-C-Si linkage(s), catalyzed by Red-Al.^{23d} Cr(CO)₆ is also known to catalyze the redistribution reactions of hydroarylsilanes.²⁴ We believe that a small portion of *n*-Bu₃SnH may be disproportionated into *n*-BuSnH₃ and *n*-Bu₂SnH₂ in the presence of Red-Al or M(CO)₆. *n*-BuSnH₃ may be immediately dehydrocoupled with *n*-Bu₂SnH₂ to produce soluble *co*-polystannane, (*n*-Bu₂Sn)_y(*n*-Bu(H)Sn)_x, of which the backbone Sn-H may subsequently undergo the cross-linking process due to the nature of very reactive Sn-H bonds. PhGeH₃ and PhSnH₃ are known to undergo the dehydrocoupling process, catalyzed by the group 4 metallocenes, to give the cross-linked polymers unlike PhSiH₃.^{24,25} We tentatively assign the polymer as a copolymer. We are making our effort to elucidate the structure of the copolymer using solid-state ¹³C and ¹¹⁹Sn NMR spectroscopy and other analytical techniques. The TGA ceramic residue yield at 400 °C of Tilley's uncross-linked poly(*di-n*-butylstannane) is 18% with onset temperature for decomposition of 255 °C,¹⁴ whereas the TGA ceramic residue yield at 400 °C of our cross-linked poly(*di-n*-butylstannane) is 38% with onset temperature for decomposition of 300 °C. The TGA data of our insoluble polystannanes show that the ceramic residue yields are consistently lower than the theoretical yields (i.e., Sn/SnC₈H₁₈=51%), probably due to loss of some volatile tin-constituents formed under the pyrolysis conditions although the polystannanes have a cross-linked structure. Hexabutyldistannane has been used in the organic synthesis as a radical initiator.²⁶ The reactions of hexabutyldistannane with various transition metal complexes are under investigation and the results will be presented elsewhere.

Conclusions

The sterically bulky tri-*n*-butylstannane *n*-Bu₃SnH was slowly transformed by the group 4 Cp₂MCl₂/Red-Al (M=Ti, Zr, Hf) and the group 6 M(CO)₆ (M=Cr, Mo, W) catalysts to produce two phases of products: one is a cross-linked solid, polystannane in 7-23% yield as minor product *via* redistribution/dehydrocoupling combination process, and the other is an oil, hexabutyldistannane in 69-90% yield as major product *via* simple dehydrocoupling process. One might naturally think that the redistribution/dehydrocoupling combination process first produced a low-molecular-weight oligostannane possessing partial backbone Sn-H bonds which then underwent an extensive cross-linking reaction of backbone Sn-H bonds, leading to an insoluble polystannane. This provides first example of redistribution/dehydrocoupling of tertiary stannane catalyzed by early transition metal complexes.

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